DOMAIN GROWTH AND RHEOLOGY IN PHASE-SEPARATING FLUIDS(Session III : Complex Fluids, The 1st Tohwa University International Meeting on Statistical Physics Theories, Experiments and Computer Simulations)

AUTHOR(S):

Onuki, Akira

DOMAIN GROWTH AND RHEOLOGY IN PHASE-SEPARATING FLUIDS

Akira Onuki
Department of Physics, Kyoto University, Kyoto 606, Japan

We first examine the condition of bicontinuity in spinodal decomposition in two component fluids. We then apply shear to such two phase states and predict some rheological properties arising from large deformatins of domains. Detailed discussions will be given to slipping layer formation and nucleation in sheared polymer solutions.

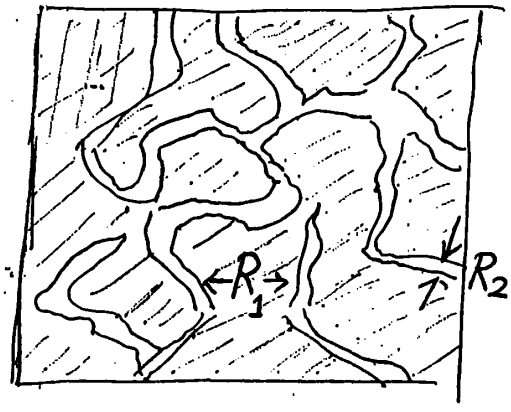
Condition of Bicontinuity in Spinodal Decomposition

Let us suppose a bicontinuous domain structure in the course of spinodal decomposition of viscoelastic fluid mixtures. When the emerging two phases have different viscosities with $\eta_1 > \eta_2$, the condition of bicontinuity of the domain structure is obtained as[1]

$$\phi_1/\eta_1 \sim \phi_2/\eta_2 \tag{1}$$

where ϕ_1 and $\phi_2 = 1 - \phi_1$ are the volume fractions of the two phases. In Fig.1 we show such a domain structure. This relation has been known as an empirical law for polymer mixtures in

Figure 1



the engineering literature. Notice that balance of the shear stress at the interface yields $\eta_1\dot{\gamma}_1 \sim \eta_2\dot{\gamma}_2$, where $\dot{\gamma}_1$ and $\dot{\gamma}_2$ are the typical magnitudes of the velocity gradients in the two phases. This suggests that domains of the first phase tend to take closed shapes because those of the second phase are more easily deformed into extended shapes. In particular, in the limit $\eta_2 \ll \eta_1$, the second phase forms thin layers enclosing the first phase. Let R_1 be the typical domain size of the first phase. Then, because the second phase is compressed into layers, the distance between two neighboring domains of the first phase is equal to the layer thickness and is characterized by a smaller length R_2. The two lengths R_1 and R_2 are related to the volume fractions by $AR_1 \sim \phi_1$ and $AR_2 \sim \phi_2$, where A is the surface area per unit volume. We notice that the velocity fields in the two phases, $\dot{\gamma}_1 R_1$ and $\dot{\gamma}_2 R_2$, should be both of the order of the growth rate $\partial R_1/\partial t$ of the domains of the first phase,

$$\dot{\gamma}_1 R_1 \sim \dot{\gamma}_2 R_2 \sim \frac{\partial}{\partial t} R_1 \tag{2}$$

Thus we obtain $R_1/\eta_1 \sim R_2/\eta_2$ and the condition (1).

Thus we obtain $R_1/\eta_1 \sim R_2/\eta_2$ and the condition (1).

On the other hand, the growth law may be obtained by assuming that the shear stress $\eta_1\dot{\gamma}_1 \sim \eta_2\dot{\gamma}_2$ is of the order of the force density σ/R_1 due to surface tension. It readily follows that the domain growth is governed by the larger viscosity η_1,

$$\frac{\partial}{\partial t}R_1 \sim \sigma/\eta_1 \qquad \text{or} \qquad R_1 \sim (\sigma/\eta_1)t \tag{3}$$

This is a generalized McMaster-siggia law for the case of different viscosities.

Rheology in Two Phase States

Next we apply a macroscopic, weak, stationary shear to the system. It is interesting that, even when $\dot{\gamma}$ is smaller than the stress relaxation rate $1/\tau$, rheology can be highly nonlinear in two phase sates. Because shear deforms and tears large domains, it gives rise to dynamically stationary two-phase states. There, if one phase forms a droplet phase, most droplets will be close to the break-up condition, which has indeed been confirmed in near-critical fluids[2] and ternary polymer solutions[3]. On the other hand, when the two phases are both percolated, domains are elongated into very long cylindrical shapes giving rise to a ***string phase*** as has recently evidensed by microscope image[4]. See Fig.2. Thus our domain structures and resultant rheology are very different from those of suspensions and emulsions where shear-induced deformations are usually small.

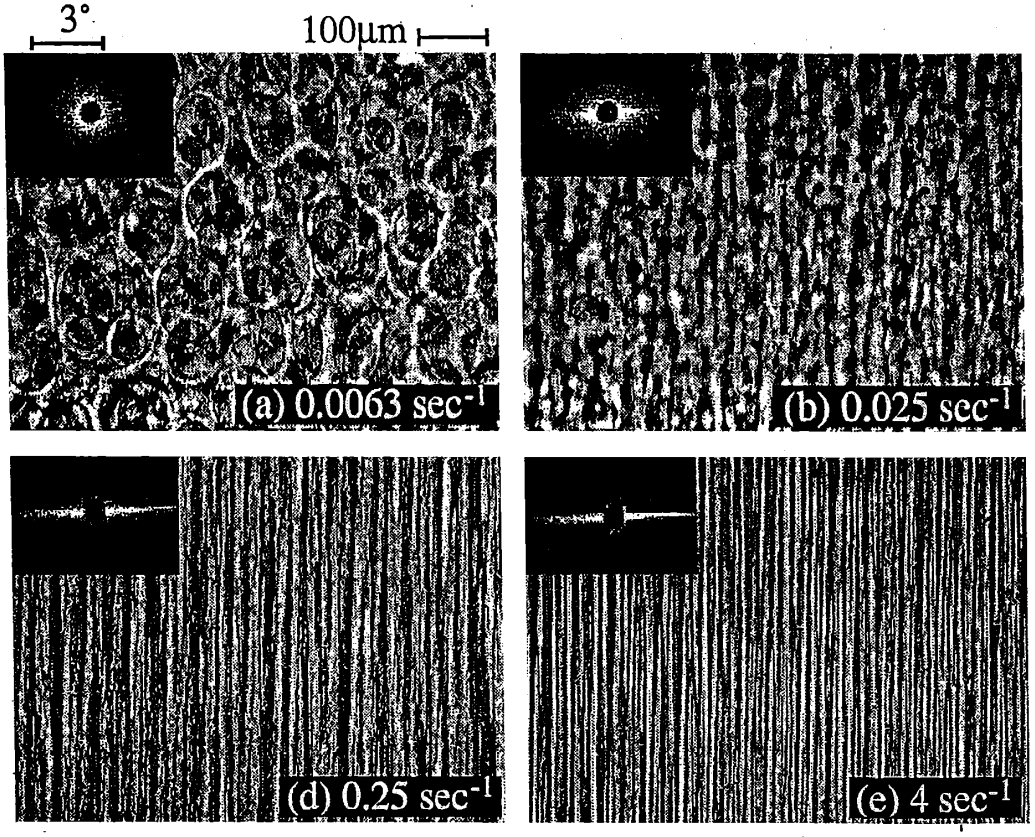


Figure 2. Transmission light micrographs and corresponding light scattering patterns (shown in the insets) obtained *in situ* in steady states of PS/PB (50:50)/DOP 3.3 wt% at ΔT=8°C. The flow direction is vertical and the bar in the inset of 1a indicates the scattering angle in air for all the patterns. The bar attached to the picture 1a is common for all the pictures.

We predict that the overall behavior of the effective viscosity η_{eff} is crudely described by the following approximate formula,

$$\eta_{eff} \sim 1/[\phi_1/\eta_1 + \phi_2/\eta_2] \tag{4}$$

When $\eta_1 \gg \eta_2$, this relation means that even a small fraction of the second phase drastically reduces η_{eff}. This is because the second phase can act as a lubricant supporting most velocity gradients unless it is very dilute. On the other hand, the normal stress differences behave as[5,6,7]

$$N_1 \sim N_2 \propto |\dot{\gamma}| \tag{5}$$

and take large maxima of order $\eta_1|\dot{\gamma}|$ even for $\eta_1 >> \eta_2$ around the bicontinuity condition[1]. This behavior arises from highly anisotropic shapes of domains and is very different from the usual behavior $N_1, N_2 \propto \dot{\gamma}^2$ in the Newtonian regime.

Bicontinuity will be realized in a wider parameter region than in the absence of macroscopic shear because elongated domains are more easily percolated in the flow direction. Here we expect formation of a string phase as has recently been observed . We stress that the domain morphology in the droplet states and that in the bicontinuous states are very different, so the rheological properties can change discontinuously, as ϕ_2 is varied, at the transition. The morphological change at the transition can be a slow process and hysteretic behavior can be expected.

Slipping Layer Formation and Nucleation in Semidilute Polymer Solutions under Shear

We limit ourselves to polymer solutions for simplicity. It is well-known that dynamic coupling between stress and diffusion gives rise to large composition fluctuations in sheared semidilute polymer solutions even above the equilibrium coexistence temperature T_{cx} for relatively large shear $\dot{\gamma}\tau \gtrsim 1$[8-11]. We point out that interesting effects of shear also arise even for very weak shear $\dot{\gamma}\tau << 1$ as the temperature is slightly lowered below T_{cx}.

We first consider the possibility of solvent layer formation at the boundary wall[12]. Let a boundary wall be wetted by solvent. Then, in the absence of shear, a macroscopic layer emerges continuously from zero as T is lowered below T_{cx}. But in the presence of shear the normal pressure $-\sigma_{yy}$ arising from the network acts on the wall and prevents the layer formation, where the x axis is in the flow direction and the y axis is in the velocity gradient direction and perpendicular to the wall. The σ_{yy} is negative, of order N_1, and proportional to $\dot{\gamma}^2$ in the Newtonian regime. Its dimensionless strength is represented by

$$C = 2(\eta/\eta_0)|\sigma_{yy}|/K \tag{6}$$

where η is the solution viscosity much larger than the solvent viscosity η_0 and $K = \phi(\partial\pi/\partial\phi)$ is the osmotic modulus. Stability analysis of steady states shows that, when $C > 1$, a slipping layer of solvent appears discontinuously as T is lowered below a certain T^* given by

$$T_{cx} - T^* = |\sigma_{yy}|/\left(\frac{\partial\pi}{\partial T}\right)_{\phi} \tag{7}$$

Namely, the layer thickness d jumps from 0 to a finite value, which is of order $(C-1)d^*$ for $C \cong 1$ and of order Cd^* for $C >> 1$, although the transient process at this transition can be very long. The slipping layer drastically changes the overall flow pattern if d exceeds $d^* = L\eta_0/\eta$, where L is the cell thickness. There appears a discontinuous change in the shear stress if the flow rate is fixed.

We introduce the supersaturation $\Delta = (T_{cx} - T)/(T_c - T_{cx})$. Then the critical radius R_c of nucleating droplets is given by $R_c = \xi_b/\Delta$, ξ_b being the blob size. The supersaturation at $T = T^*$ is of order $(\dot{\gamma}\tau)^2$ and is very small, so there is no bulk nucleation there.

We then consider the case in which the boundary wall attracts polymers and the slipping layer formation can be avoided. As T is lowered, droplets consisting mostly of solvent will emerge as nucleation. Ref.13 shows that the deformation rate of a critical droplet from sphericity is very small and is of the order of $\gamma/\eta R_c$, where γ is the surface tension. Therefore the critical droplet is not broken by shear if $\gamma/\eta R_c > \dot{\gamma}$. Using the scaling theory we may rewrite this condition as

$$\dot{\gamma}\tau < \Delta \tag{8}$$

under which we can observe appreciable droplets in a metastable semidilute region. Of course Δ should not be too small for the metastable system to overcome the nucleation barrier, the cloud point value of Δ is expected to be about 0.02. In the reverse case $\dot{\gamma}\tau > \Delta$ there is no metastability and, as T is further lowered, phase separation occurs as spinodal decomposition.

We note that an isolated droplet with a small viscosity in a viscous fluid can be much elongated prior to break-up. Therefore the shape of critical droplets should be anisotropic even for very small shear. This aspect has not yet been studied. In summary, it is of great interest how phase separation is achieved in polymers even in weak shear as well as in strong shear.

References

[1] Onuki A., Europhys. Lett., **28** (1994) 175.

[2] Min K.Y. and Goldburg W.I., Phys. Rev. Lett., **70** (1993) 3205.

[3] Hashimoto T. et al., J. Chem. Phys. **88** (1988) 5874; ibid., **91** (1989) 4369.

[4] Hashimoto T. et al., Phys. Rev. Lett., **74** (1995) 126.

[5] Onuki A., Phys. Rev. A, **35** (1987) 5149. **2** (1992) 1505.

[6] Doi M. and Ohta T., J. Chem. Phys., **95** (1991) 539.

[7] Takahashi Y. et al., **38** J. of Rheol. (1994) 699.

[8] Helfand E. and Fredrickson G.H., Phys. Rev. Lett. **62** (1989) 2468.

[9] Doi M. and Onuki A., J. Phys. II France **2** (1992) 1631.

[10] Wu X. -L., Pine D.J. and Dixon P.K., Phys. Rev. Lett. **66** (1991) 2408.

[11] Hashimoto T. et al., J. Phys. Soc. Jpn **60** (1991) 356 ; ibid. **61** (1992) 1839.

[12] Onuki A., Physica A **204** (1994) 499.

[13] Onuki A., J de Phys.II **2** (1992) 1505.